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# Irresistible Materials Multi-Trigger Resist
# "The Journey towards High Volume Manufacturing Readiness."

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## ABSTRACT

Irresistible Materials (IM) is a UK company spun out of the University of Birmingham. It is developing novel resist systems based on the Multi-trigger concept, and spin-on-carbon hardmask materials. IM has developed a new EUV resist that is non-metal based, does not need a post exposure bake (PEB), and delivers high sensitivity, excellent contact hole resolution, with low LER. It is being readied for HVM through a partnership with Nano-C, Inc. (the Massachusetts based manufacturer of advanced electronic materials and chemicals). The transition to scalability will be the highlight of this discussion.

**Keywords**: EUV Photoresist, high resolution, volume manufacturing, contacts holes, molecular, resolution.

## 1. INTRODUCTION

EUV lithography's introduction into high volume manufacturing (HVM) has been delayed by a number of technology challenges; specifically, EUV optics, EUV photomask infrastructure, and EUV photoresist materials. Speaking to the photoresist related issues, Line Edge Roughness (LER), sensitivity and resolution have been the focus areas in the search for a photoresist system that can create the smaller features enabled by EUV patterning. So far, a single EUV resist system simultaneously delivering all the key 'wants' has not been developed. As a result, the industry has had to work with a little higher LER or lower resolution or a higher patterning dose requirement.

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As we all know, the approach to photoresist development is being challenged. The earliest EUV photoresists were modified DUV and/or 193nm based polymer platform photoresists. But, these photoresist extensions did not have the required sensitivity, LER or resolution. Advanced Device Manufacturers (ADMs) and Scanner suppliers have urged the photoresist suppliers to consider new photoresist systems.

One of the new photoresist platforms that rose to prominence has been given the name 'molecular resist' because they represented a departure from polymer based photoresist suspensions to formulations based around 'small molecules'. There are a number of molecular systems currently being investigated ranging from metal oxides[1] Hafnium core nano particles,[2] metal complexes[3], molecular glasses, and the material discussed here[4–6], which is the evolution of IM's work with molecular resists, the Multi-Trigger Resist system.

As important as developing a new photoresist system is to EUV introduction, what is more important is its manufacturability; can it be scaled with low metallic ion contamination, will scaling be cost effective and can manufacturing volumes be purchased quickly. This sounds easy, but it is not. Raw materials need to be investigated, multiple raw material suppliers need to be developed, synthesis techniques need to be perfected, and manufacturing level formulation needs to be rendered reproducible day-to-day (e.g., lot to lot consistency of the photoresist batches).

The authors of this paper will focus on the steps that IM has taken to make its new low cost of ownership HVM photoresist solution ready for HVM customers.

## 2. EXPERIMENTAL

The resist samples were prepared by dissolving the individual components in ethyl lactate. The resist was then spun onto a proprietary carbon under-layer developed by IM. On occasion, for instance in contact hole patterning, the photoresist is spun on bare silicon wafers where the coatings are well deposited and uniform.

After spin coating the resist, the samples received a post application bake. All EUV exposures presented here were performed using the Berkeley Microfield Exposure Tool (MET). After exposure, the samples received an optional post exposure bake and were developed in n-butyl acetate for 60 seconds followed by an MIBC rinse. However, IM has also discerned that patterning performance is not adversely impacted when no PEB is used. In fact, IM believes that the PEB can now be eliminated, a key advance in overall productivity.

Exposed samples were analyzed with a scanning electron microscope (SEM) in top-down view. Critical dimension (CD) and LER were calculated from the SEM images with the commercial SuMMIT software package. The doses were used as provided by the relevant tool provider.

## 3. DISCUSSION

IM has developed a new approach to achieve high-resolution, high sensitivity, and a low LER resist– the Multi-Trigger Resist. In a multi-trigger material, resist exposure proceeds via a catalytic process in a similar manner to a chemically amplified resist. However, instead of a single photoacid causing a single resist exposure event and then being regenerated, in the multi-trigger resist multiple photoinitiators activate multiple acid sensitive molecules, which then react with each other to cause a single resist event while also regenerating the photoinitiators. In areas with a high number of activated photoinitiators (higher dose areas, for instance at the centre of a pattern feature) resist components are activated in close proximity and the multistep resist exposure reaction proceeds, ending with photoinitiator regeneration and thus further reactions, ensuring high sensitivity. In areas with only a low number of activated photoinitiators (lower dose areas, for instance at the edge of a pattern feature), the activated resist components are too widely separated to react and active photoinitiators are thus removed, stopping the catalytic chain. The multi-trigger resist creates an increase in the chemical gradient at the edge of patterned features, and reduces undesirable acid diffusion out of the patterned area. The picture below details how the multi-trigger approach departs from the traditional approach used in 193nm/248nm photoresist extension materials used for EUV patterning (figures 1 & 2).

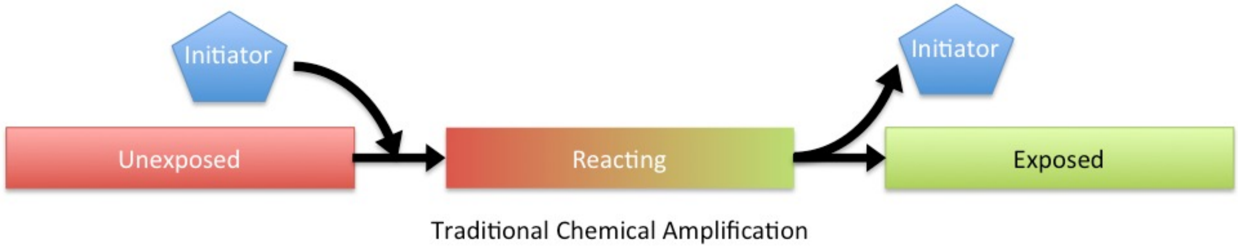



**Figure 1: Schematic demonstrating traditional chemical amplification. An initiator such as a photoacid reacts with a photoresist molecule—to change its solubility or cause crosslinking—and is regenerated to allow further reactions.**

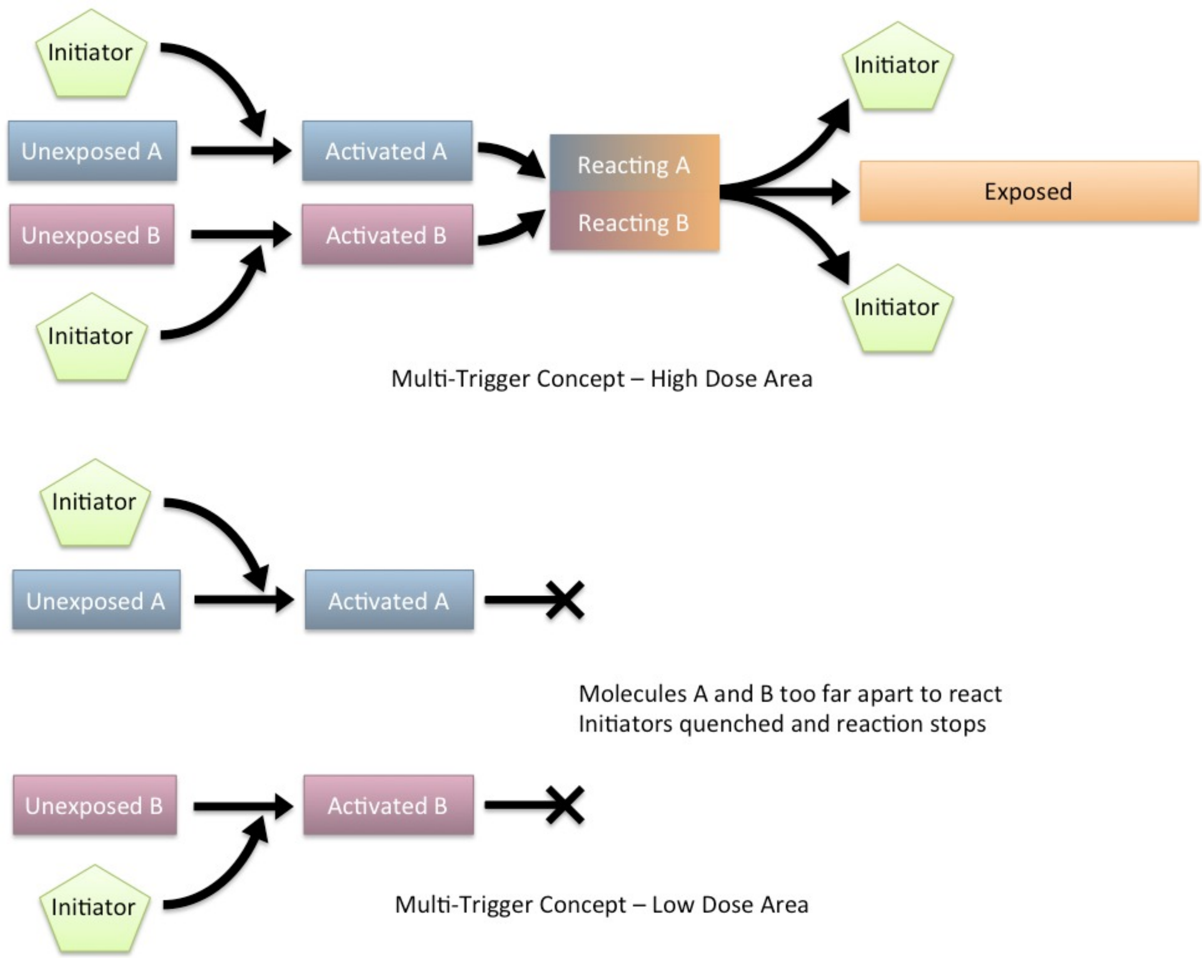



**Figure 2: In a multi-trigger resist the initiator activates a resist molecule but is not immediately regenerated. If two resist molecules are activated in close proximity then the reaction proceeds as normal leading to a resist exposure event and initiator regeneration. In low dose areas the initiators are not regenerated leading to enhanced chemical contrast at feature edges.**

### 3.1 The Approach

### 3.2 Outgassing tests results

New EUV photoresist platforms have been required to show that they have suitable outgassing performance in order enable testing on NXE 3100/3300 systems. Outgassing studies utilizing xMT, undertaken on the IMEC outgassing tools, have shown that both cleanable (<2.5 nm) and non-cleanable (see figure 15) outgassing are well within spec for the NXE 3300.

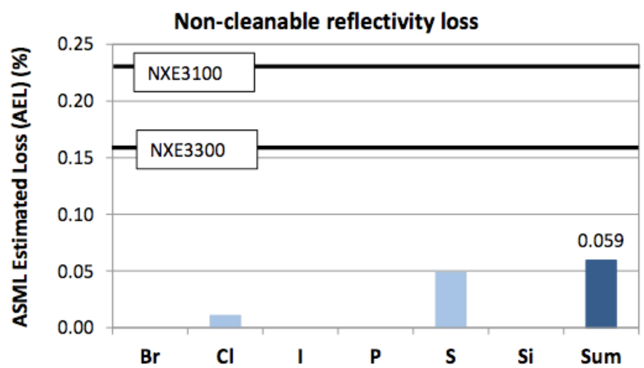


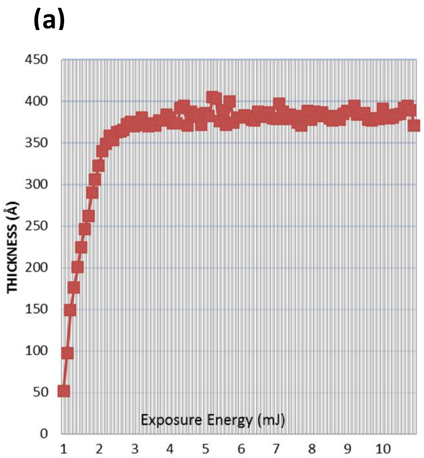

**Figure 3: IM / Nano-C Development to Manufacturing scale-up flow**

### 3.3 Drain waste tests

A precipitation test was carried out at Bio Ma-Tek using waste drain solvents from a fabrication facility and IM xMT-213 resist. The resist passed the precipitation test with no precipitate optically visible at the specified test points of 0 hours, 8 hours, 24 hours, 3 days and 7 days. Dynamic Light Scattering using a Malvern Instruments Zetasizer Nano ZS was also carried out on the seventh day. This showed the intensity weighted size distribution having three peaks at 14 nm (36%), 420 nm (60%) and 5040 nm (2%). These results indicate that the IM resist can be used within a fabrication facility with no precipitation issues.

### 3.4 Exposures using 193nm dry illumination

It has been reported that the xMT resist performs well under electron beam lithography at energies ranging between 30 – 100keV. Initial testing has now demonstrated that the platform shows high sensitivity under 193 nm dry illumination. Figure 3a shows the response curve – dose to gel is ~ 2 mJ/cm$^2$. Features with a CD of 80 – 100 nm have been patterned in initial testing, using a 40nm film thickness (exposure latitude is shown in figure 3b), holding out the possibility that xMT can provide a single resist solution to hybrid patterning approaches incorporating 193 nm, EUV and electron beam patterning.




(b) Exposure Latitude

| Dose (mj/cm) | 4 | 4.2 | 4.4 | 4.6 | 4.8 | 5 | 5.2 | 5.4 | 5.6 | 5.8 | 6 | 6.2 | 6.4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CD (nm) | 80.71 | 86.9 | 91.24 | 93.56 | 94.9 | 103.6 | 102.94 | 113.03 | 110.83 | 108.26 | 115.28 | 117.46 | 121.65 |

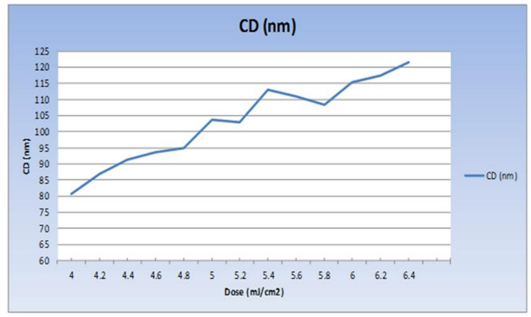



**Figure 4a: Dose to gel in 193 nm dry exposure is ~ 2 mJ/cm$^2$, and (b) On this test, 100 nm lines were patterned at a dose of 5 mJ/cm$^2$**

### 3.5 Patterning dense line/spaces with a target dose of 20 mJ/cm$^2$

The next stage of optimization using the facilities at the Berkeley Microfield Exposure Tool involved changing the formulation to increase the sensitivity. This was achieved by the addition of a highly absorbing high-Z additive into the xMT resist system. The quencher level was also reduced. Samples were run with the HB2 hybrid formulation, without a PEB. The mask was the Pseudo PSM 2D DF mask with F2X illumination. 18 nm half pitch and 16 nm half pitch lines were patterned with a sub 20 mJ/cm$^2$ dose.

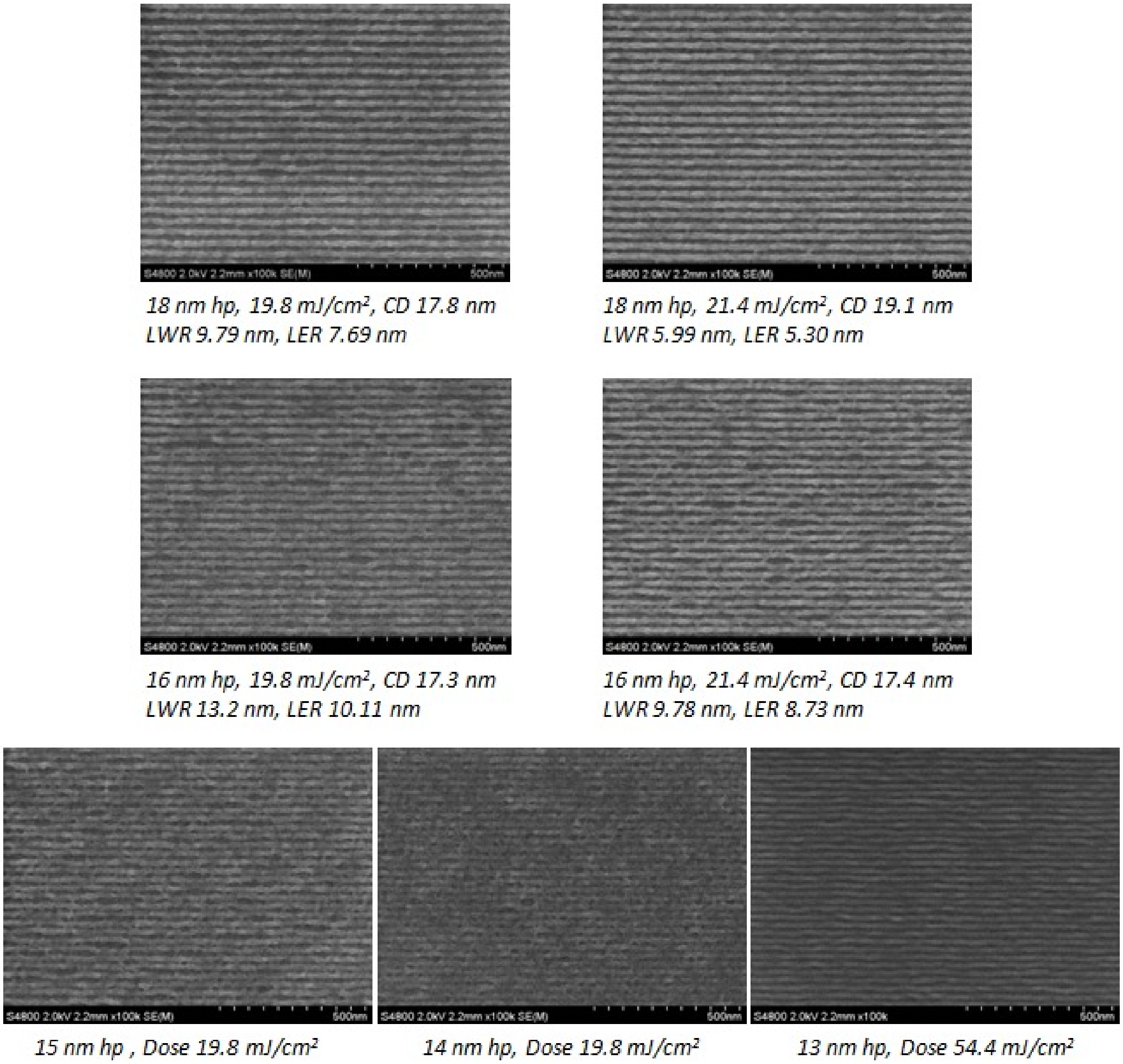



**Figure 5 Images of lines patterned using F2X 2D mask**

### 3.6 Contact hole evaluation

IM have developed their resist system to the point that is has produced outstanding contact hole performance using a very low exposure energy. The plots below show outstanding dose sensitivity ~10 mJ/cm$^2$ while resolving contact holes that measured less than 30 nm (see figure 6 below.)

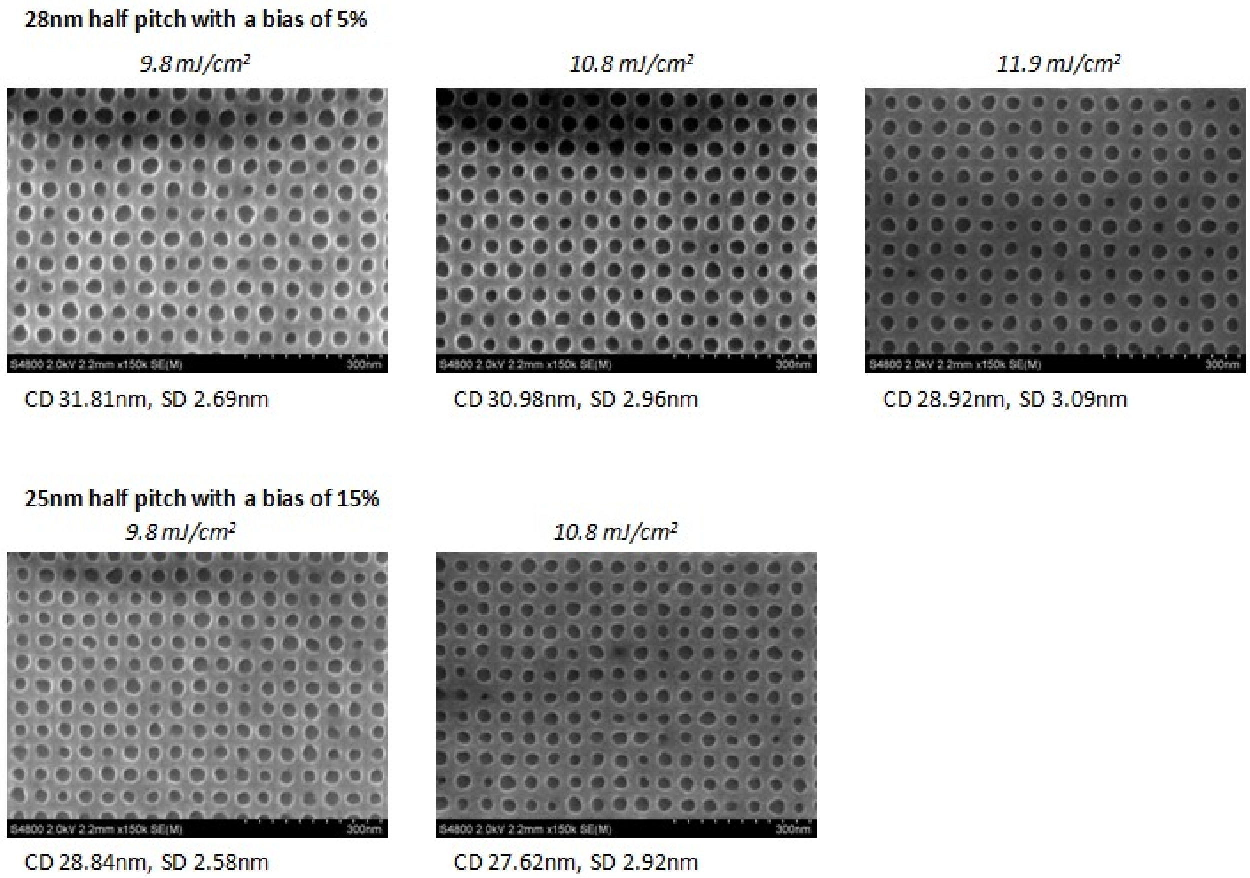



**Figure 6 28nm and 25nm half pitch contact holes patterned at 9.8 mJ/cm$^2$ to 11.9 mJ/cm$^2$**

The images and results shown in figure 7 indicate that the resist has a wide depth of focus with consistent results over a 200nm change in focus. The standard deviation is higher for the lower biased, smaller holes. This means that increasing the size of the holes, whilst maintaining the same pitch, results in more uniform holes with less defects, as would be generally be expected.

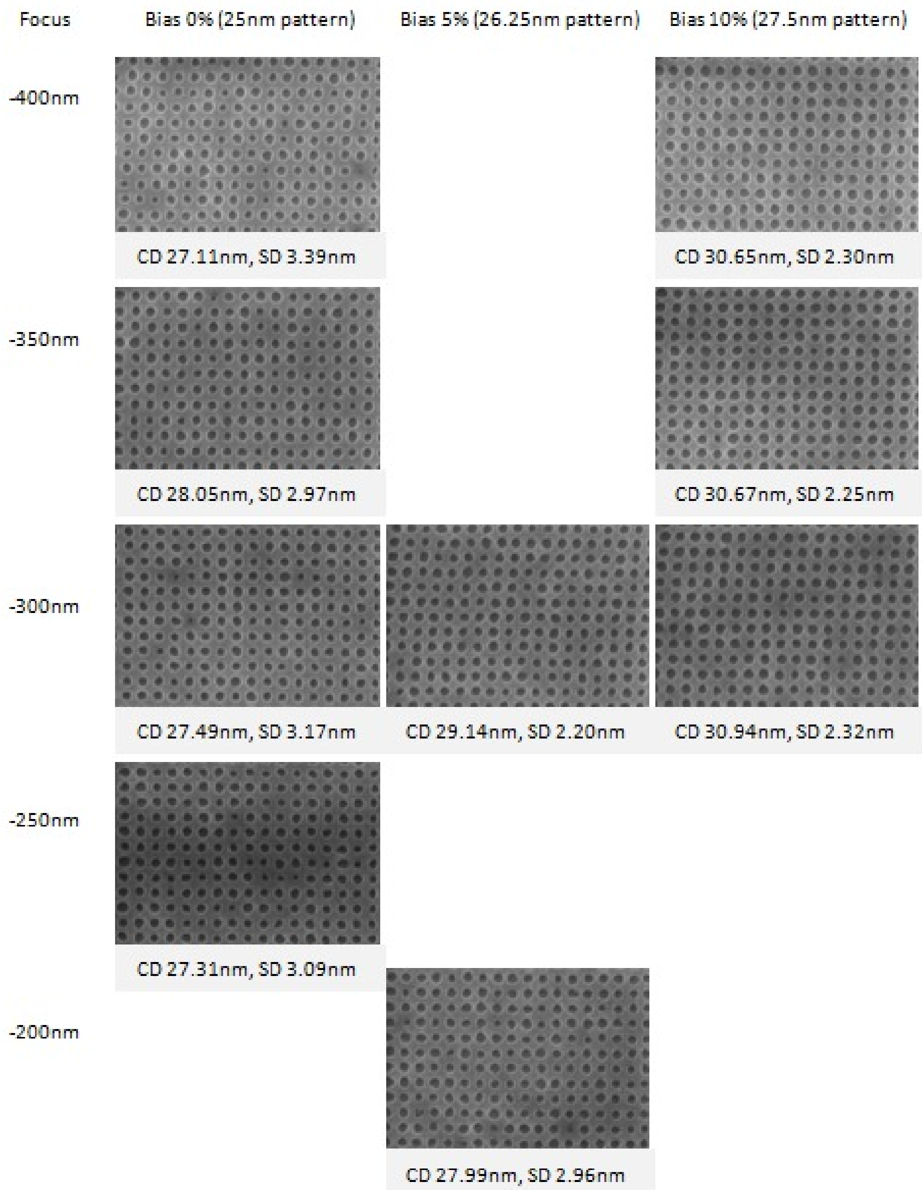



**Figure 7 Focus and Bias Matrix at 25nm half pitch and a dose of 11.4mJ/cm$^2$**

### 3.7 Status of metallic ion management

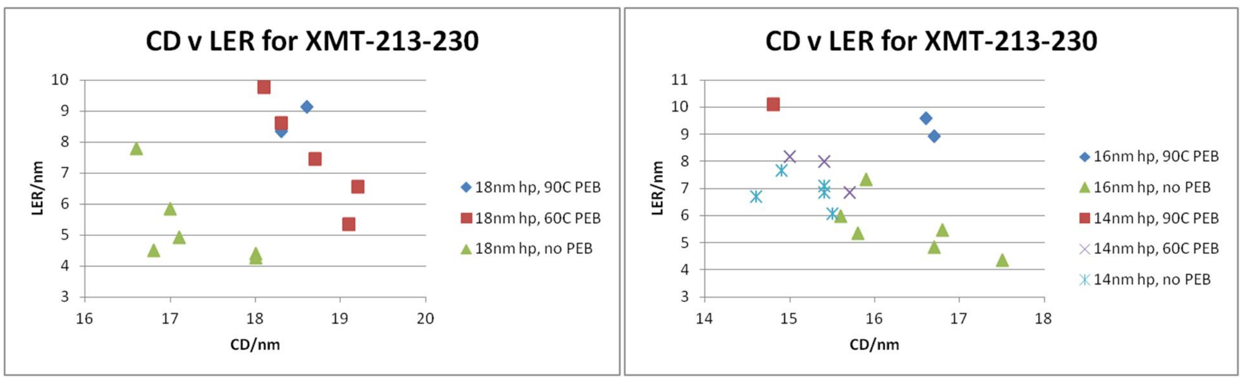
Metallic ion migration is a key concern for advanced device manufacturers. IM recognizes the sensitivity of devices to migrating ions that might be resident in photoresist formulations and therefore has implemented several protocols to address metal ion related concerns. First, IM is working closely with raw material suppliers so that 'raw' are purchased with low metallic ions. Next, tight control of packaging containers assures no contamination results from the packaging. IM has developed a number of techniques to reduce metallic ion contamination resulting from the manufacturing process. So far, excellent results have been obtained, see the chart below which shows typical performance to date. The Nano-C team believes they can drive metals even lower with larger volumes. I have highlighted the values that would be considered out of specification at above 10ppb; Nano_C has an action plan (with high certainty) to reduce these marginally 'out of spec' values. The IM and Nano-C team are comfortable that these values would be in specification for gallon purchases.

| Metal | | Detection Limits (ppb) | Post purification metal levels (ppb) |
|---|---|---|---|
| Aluminum | (Al) | 5 | <5 |
| Barium | (Ba) | 1 | 1.6 |
| Beryllium | (Be) | 5 | <5 |
| Bismuth | (Bi) | 5 | <5 |
| Cadmium | (Cd) | 1 | <1 |
| Calcium | (Ca) | 5 | 8.5 |
| Chromium | (Cr) | 1 | 9.3 |
| Cobalt | (Co) | 1 | <1 |
| Copper | (Cu) | 5 | <5 |
| Gallium | (Ga) | 1 | <1 |
| Iron | (Fe) | 10 | 11 |
| Lead | (Pb) | 1 | <1 |
| Lithium | (Li) | 1 | <1 |
| Magnesium | (Mg) | 1 | 7.2 |
| Manganese | (Mn) | 1 | <1 |
| Molybdenum | (Mo) | 1 | 5.9 |
| Nickel | (Ni) | 5 | <5 |
| Potassium | (K ) | 20 | <20 |
| Sodium | (Na) | 5 | 50 |
| Strontium | (Sr) | 1 | <1 |
| Thallium | (Tl) | 5 | <5 |
| Tin | (Sn) | 1 | 5.1 |
| Titanium | (Ti) | 2 | 4.0 |
| Zinc | (Zn) | 5 | 9.8 |
| Zirconium | (Zr) | 1 | <1 |

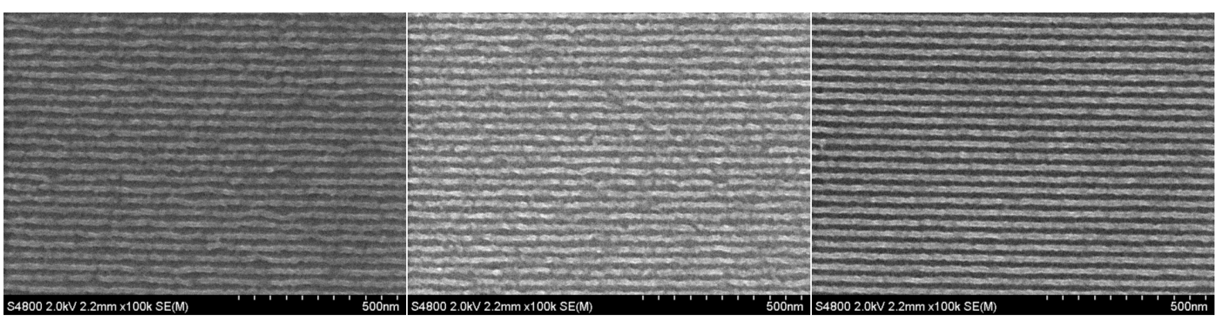
**Figure 8 ICP-MS data showing metal contaminant levels after purification (randomly selected)**

### 3.8 Status of metallic ion management

As mentioned above, this photoresist system does not require a post exposure bake. A study was conducted using 16nm and 18nm lines and spaces, as the metric, (thereby making it easier to evaluate LER and pattern stability) measuring CD and LER change with PEB. The LER appeared to improve when the post exposure bake was eliminated (see figures 9). Figure 10 shows 18nm lines at two post exposure bake conditions and with no post exposure bake. The patterns with no post exposure bake seem greatly improved verse the patterns that have received no post exposure bake.




**(Figure 9) CD and LER with and without PEB**




90°C PEB 60°C PEB no PEB

**(Figure 10) 18nm SEM Micrographs with and without PEB**

## 4. CONCLUSION

IM has developed a new ultra-sensitive resist material that is not metal based, nor does this system require the use of a PEB. The resist system is based on a new chemistry IM called the 'Multi-Trigger Resist system'. This new chemistry delivers these key benefits and has delivered high sensitivity, high resolution, and a lower total cost of ownership because it does not require the extra process time need for post exposure bake. Another benefit of the elimination of the post exposure bake step is the improved flexibility gained by the EUV track. Reiterating, IM has demonstrated performance of 25nm contact holes at an exposure energy of 11.4 mJ/cm$^2$ on 0.3NA Berkeley Micro Exposure System. The exciting results have attracted much interest from NXE 3300 users and we have already begun to design test plans to help them evaluate this new IM resist system.

IM believes this material will lower the cost of ownership for users by the elimination of the post exposure bake and the low patterning energy. The process for assuring low metallic ion concertation has already been dialed in by Nano-C, as has the path to scaling up the production of this resist system. Another, inherent, benefit of this system is that it is carbon based; therefore the existing and well understood etch processes can be used to transfer patterns using this material. Very little etch process development is expected to be required in order to implement this resist system.

The metallic ion concentration has been driven to a level that makes it clear to see that the photoresist is naturally quite low in ion contamination. The few materials that are currently reading "slightly out of specification" are within reach of further reduction in the photoresist pilot line.

Nano-C, has produced multiple lots of the photoresist, and are well positioned to scaling up to larger batches. Current volumes are sufficient for customer pilot line use and there is a clear path forward to larger scale production volumes when they become necessary.

Thus, IM believes it has developed a low cost of ownership, high sensitivity, highly resolving, no PEB photoresist that can leverage existing user infrastructure (etch processes and gases) and satisfy both EUV and 193nm patterning requirements. Thus we believe this photoresist system is ready for pilot line introduction.

## ACKNOWLEDGEMENTS

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